

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 85200620.4

(51) Int. Cl.⁴: **C 05 G 3/00**
A 61 K 9/32, B 01 J 2/30

(22) Date of filing: 19.04.85

(30) Priority: 27.04.84 NL 8401362

(43) Date of publication of application:
08.01.86 Bulletin 86/2

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

(71) Applicant: **NEDERLANDSE CENTRALE ORGANISATIE
VOOR TOEGEPAST-NATUURWETENSCHAPPELIJK
ONDERZOEK**
Juliana van Stolberglaan 148
NL-2595 CL The Hague(NL)

(72) Inventor: **Huizer, Leendert**
Carolinenberg 13
NL-2716 EP Zoetermeer(NL)

(74) Representative: **van der Beek, George Frans et al,**
Nederlandsch Octrooibureau Johan de Wittlaan 15 P.O.
Box 29720
NL-2502 LS 's-Gravenhage(NL)

(54) Solid substrate which consists at least partially of a biologically or chemically active substance and is coated with a (meth)acrylic polymeric network as well as a process for providing said coated substrate.

(57) A solid substrate, which contains or consists of a biologically or chemically active substance, is coated with coating material containing at least one polymerizable crosslinkable polyfunctional acrylic or methacrylic compound whereafter the coating material is subjected to polymerization substantially in the absence of non-polymerizable components to form a network coating of polymer on the surface of the solid substrate. This coating permits either the controlled release of active substance from the coated substrate or the controlled access of material reacting with said active substance into the coated substrate and the controlled release of the resulting reaction products from the coated substrate.

EP 0 167 184 A1

Solid substrate which consists at least partially of a biologically or chemically active substance and is coated with a (meth)acrylic polymeric network as well as a process for providing said coated substrate.

5 The invention relates to a substrate which consists at least partially of a biologically or chemically active substance and at least part of the surface of which is coated with a permeable network coating of a polymer. This coating permits either the controlled release of active substance from the coated substrate or the controlled access of
10 material reacting with said active substance into the coated substrate and the controlled release of the resulting reaction products from the coated substrate. The invention also relates to a process for providing said coated substrate.

15 It is known to provide substrates containing an active substance with a coating permitting the active substance to be released to the environment in a controlled manner.

 Coating particulate fertilisers in this way is generally known. Reference may be made to a review article in Ullmanns Enzyklopaedie der technischen Chemie, 4th edition, volume 10 (1975), page 233 and to the
20 literature cited therein. According to British Patent No. 750,807, a fertiliser is, for example, mixed with a solution of a polymer of a polar vinyl compound in an organic solvent. After removal of the solvent, the particles are found to be coated with a layer of the polymer.

25 It is known from German Patent 1,248,687 that fertilisers can be coated using aqueous solutions which contain a mixture of a precondensate of from 20 to 80% by weight of an aminoplast precondensate and 80 to 20% by weight of a copolymer of from 50 to 90% by weight of an ester of acrylic acid or methacrylic acid with a monovalent,
30 non-polymerizable alcohol, 5 to 30% by weight of an α,β -ethylenically unsaturated mono- or dicarboxylic acid and 2 to 45% by weight of other monomeric copolymerizable compounds, whereas according to German Patent 1,250,456 an aqueous solution of a mixture of from 20 to 80% by weight of an aminoplast precondensate and 80 to 20% by weight of a polyester
35 component is used. After the coating of the fertilisers with the aqueous solutions, the components of these solutions harden to form a coating layer on the fertiliser particles.

 For coating fertiliser particles, according to German

patent applications Nos. 1,242,573 and 1,254,162, copolymers of dicyclopentadiene and drying or semi-drying oils are used, and according to German patent application No. 1,270,579, drying oily polyene polymers, which are isomerised under the influence of catalysts and are dried after application onto the particles. are used.

According to German Patent No. 1,467,383, a mixture of a polyene polymer containing free vinyl groups with a drying oil and a lipophilic aminoplast condensate is used. According to German Patent No. 1,592,655 organic substances, which swell in water, or finely divided salts, oxides and/or metals are incorporated in plastic coatings which are intended for coating fertiliser particles. According to French Patent No. 2,253,553, a plastic which is degradable under the influence of ultraviolet light is used for coating fertilisers.

From Chemical Abstracts, vol. 78 (1973), page 410, abstract 28544g it is known to mix fertiliser granules with an aqueous acrylamide solution and to expose the mixture to γ -radiation thus giving a polymerized slow release fertiliser with low hygroscopicity. However, by this process a water soluble coating of a linear polymer is formed upon the fertiliser granules, which does delay the release of the fertiliser into the soil after the fertiliser granules have been brought therein, but does not permit the controlled release of the fertiliser for an extended period of time. Once the polyacrylamide has been dissolved from the granules the whole fertiliser content of the granules becomes active immediately.

It is likewise known to coat drugs with polymers in order to ensure that the release of the drug in the gastro-intestinal tract can be controlled accurately. Reference may be made to Kirk-Othmer's Encyclopedia of Chemical Technology, 3rd edition, volume 17 (1982), page 304 and to the literature references cited therein.

In the processes for coating particles to permit the controlled release of an active substance as described hereinabove, aqueous or organic solutions of polymers as well as oily mixtures have been used. The disadvantage of these known processes is that the solvent must be removed or drying and hardening must be effected for a fairly long time. In the course thereof, a state always occurs in which the coating of the particles is viscous and/or tacky, as a result of which the particles adhere to each other, which leads to the formation of agglomerates as well as to the damage of the coating layer applied. The disadvantage of

damaging the coating layers can, it is true, be overcome by applying more than one such layer, but the disadvantage of the possibility of agglomerate formation still persists.

5 The disadvantage as described hereinbefore is also encountered when using the process of the French Patent 1,081,591 for coating granules of hygroscopic substances. In this process small amounts of a polymeric vinyl compound are added to these granules, which vinyl compound is generally dissolved in water or an organic diluant or suspended or emulsified in water. The resulting coating prevents the agglomeration of 10 the hygroscopic granules. According to the French Patent No. 1,081,591 it is also possible to add the vinyl compound as a monomer to the granules and then polymerize it in situ. However, the disadvantage of this embodiment is that the vinyl compounds used are liquids with a very low viscosity, so that a considerable amount of vinyl compound must 15 be used to obtain a sufficient coating, which coating moreover will appear to be very irregular. If one would use this process for coating granules containing an active substance, which should be released to the environment, the release will be unsatisfactory in view of the thick layer, which moreover does not form a proper network.

20 It is further known from the USSR Patent No. 543.250 to treat fertiliser granules with a monomer or a monomer mixture in the gas state. An example has been given of coating urea granules by contacting them with a methylmethacrylate vapour whilst subjected to γ -radiation at 60°C. In this way a coating of a linear polymer is formed upon the 25 granules, which does delay the release of the fertiliser, but is not satisfactory to control the release of the fertiliser from the granules. If the process described in this USSR Patent would be used with liquid methylmethacrylate the same disadvantages would be encountered as described with the process of the French Patent No. 1,081,591, namely 30 that in view of the very low viscosity of the methylmethacrylate a very thick and/or irregular coating would be formed upon the granules, which is not suitable either for permitting controlled release of the fertiliser to the environment.

It is known from the British Patent No. 1,269,018 to coat 35 pulverulent materials with a polymer by subjecting the pulverulent material to a high frequency electrical discharge under reduced pressure in the presence of at least one polymerizable organic compound which is in the liquid or gaseous state or may be dissolved

in a solution. As examples of polymerizable compounds monomers having a very low viscosity are mentioned. A great amount of said monomer is necessary to form a complete coating and said complete coating is too thick to permit the desired controlled release of active substance
5 present within the coating of the polymer.

It has now been found that a solid substrate, which consists at least partially of a biologically or chemically active substance and at least part of the surface of which is coated with a permeable network coating on the base of a water insoluble acrylic or methacrylic
10 polymer, has very desirable properties with respect to the possibility of the controlled release of the active substance present or with respect to the controlled access of material reacting with said active substance into the coated substrate and the controlled release of the resulting reaction products from the coated substrate. The process which
15 provides such a coated substrate does not make use of polymer solutions or emulsions. The process comprises contacting the surface to be coated of the solid substrate with a coating material containing at least one polymerizable crosslinkable polyfunctional acrylic or methacrylic compound and subjecting the coating material to polymerization
20 substantially in the absence of non-polymerizable components.

Since the process according to the invention is carried out in the substantial absence of non-polymerizable components, there is no need of removing volatile compounds, such as solvents.

The substrates to be coated may be of any shape and dimension.
25 In practice in general fibers, films and especially granules containing active substances will be coated. It is not always necessary or desirable to coat the complete surface of the substrate containing the active substance. This substrate can e.g. be anchored upon solid supports and in that case only the surfaces exposed to the environment
30 should be coated. The way of coating, the thickness and the strength of the resulting coat are in most cases determined by the nature of the active substance in the substrate.

The biologically or chemically active substance which is present in or forms the substrate can in fact be of any nature. Examples of
35 these substances are drugs of any kind, flavouring agents, fragrances, agrochemicals, such as herbicides, insecticides, fungicides, nematocides, fertilisers, soil improving agents, plant growth regulators etc. In many cases the coating is applied not to pure active

substances, but to preparations or formulations of these active substances. The formulations or preparations may contain any of the known diluents. surface active agents and other additives known in the art. The active substances as described hereinabove can be released
5 from the coated compositions in a controlled way.

It is further feasible to coat solid catalyst compositions with an acrylic or methacrylic polymer so as to make it possible that the catalyst deploys its activity in a controlled way, being released to the system to be catalyzed only gradually. The same holds for solid
10 enzyme containing compositions, which might be coated in such a way that the enzyme is hold back within the coating, but a medium, preferably a liquid medium, such as an aqueous medium, which contains the substance to be subjected to the action of the enzyme, is admitted from the outside into the coated composition, which then releases in a
15 controlled way to the environment of the product obtained by the enzymatic action in the medium. Similar considerations apply to solid compositions containing micro-organisms. bacteria etc. It therefore appears that the substrate may also contain the active substance immobilized. In these cases it is the medium of the environment, which
20 will be in most cases liquid, but which may also be gaseous. that penetrates through the network coating, acts upon or reacts with the active substance and transports resulting products outside of the coating solid substrate. The broad spectrum of possibilities of coating solid substrates is based on the substantially unlimited variability of
25 the type and structure of the network formed on the substrate as described in the above, which means that for any specific purpose a suitable coating can be developed by varying the types and/or proportional amounts of the ingredients of the coating material.

The acrylic and methacrylic compounds used in the process of the
30 invention are called polyfunctional, because the suitable coating materials must have two or more (meth)acrylic groups, since otherwise they do not form a network upon polymerisation. Thus, compounds such as acrylamide or methylmethacrylate are not suitable. Suitable compounds may e.g. be represented by the general formulae $R-(-CO-C=CH_2)_n$ or
35 $R-(-CO-C(CH_3)=CH_2)_n$. In these formulae n represents an integer of at least 2 and is preferably 2, 3 or 4. R is e.g. the moiety of a polyalcohol or polyamine, with which the (meth)acryl moieties form the coating material. This polyalcohol or polyamine may be a monomeric

compound, e.g. 1,6-n-hexanediol, trimethylolpropane or pentaerythritol or similar amine compounds, an oligomeric compound, such as a dimeric, trimeric or tetrameric compound, or a more complex reaction product as may appear from the specific examples given hereinafter. These coating materials are in some cases prepolymers having specific (meth)acrylic functionalities. All (meth)acrylic polymers will be further referred to as (meth)acrylates, also when they could be considered as amides.

A number of the coating materials useful in the process of the invention is known. However, these known compounds have not been used for the present purpose. Examples of known coating materials, which are suitable for the process of the invention are urethane-acrylates, such as those marketed under the trademarks Ebecryl (UCB, Drogenbos, Belgium) and Photomer (Diamond Shamrock Corp.), epoxy-acrylates, such as those marketed under the trademarks Ebecryl, Photomer and Laromer (BASF, Ludwigshafen, Federal Republic of Germany) and VPS (Degussa, Frankfurt, Federal Republic of Germany), polyester-acrylates, such as those marketed under the trademark Laromer, polyether-acrylates, as well as amine-acrylates, such as those marketed under the trademark Uvecryl (UCB, Drogenbos, Belgium). These (meth)acrylates are liquid products.

The viscosity of the coating materials which hereinafter are also referred to as lacquers, is very important. If the viscosity is too low, the lacquer used is too thin and the coat applied is quickly damaged. If the viscosity is too high, the particles can easily adhere to each other. The most suitable viscosity is also determined by the coating technique employed and by the type of the substrate coated. Therefore, absolute quantitative data for the viscosity are difficult to give. In practice an expert can determine the most suitable viscosity by means of simple tests. The viscosity can also be adjusted by using mixtures of coating materials, in which case it is also true for each mixture that it influences the rate of release of the active substance from the substrate or the access of reacting medium into the substrate.

The thickness of the final lacquer coat is dependent on the type of the coating material and/or of the substrate used and on the rate of release desired and may be varied within wide limits, for example, between 5 and 100 μm . Said thickness can be easily determined by the expert in the art.

Examples of low viscosity coating materials are triisopropylenglycoldiacrylate, 1,6-n-hexanedioldiacrylate and

trismethylolpropanetriacrylate. These acrylates are copolymerized with the more viscous acrylates, which can be solved therein.

In a number of cases it may be advantageous to incorporate in the coating material one or more monofunctional polymerizable monomers so as to modify the properties of the coating material or of the resulting coat. These monofunctional compounds, which may also be (meth)acrylates, as such do not form a network, when subjected to polymerization, but modify the network formed by the polyfunctional (meth)acrylates with which they are copolymerized. Examples of such monofunctional monomers are acrylic acid, methacrylic acid, (meth)acrylic esters, N-vinylpyrrolidone, vinylpyridine and styrene. These compounds copolymerize with the crosslinkable acrylates or methacrylates or are at least immobilized in the coating layer obtained upon the substrate.

During coating, a network is formed upon the surface coated. Determining factors for the effectiveness of the network in the controlled release of active substance from the substrate are, inter alia, the polarity of the crosslinked coating layer, the rigidity or mobility of the polymer chains in the network, the mesh width in the network and the manner in which the material of the network reacts upon the environment into which the coated substrates are introduced. Thus, for example, when using a coating layer which has a slightly polar character, release of an active polar substance from the substrate as a rule occurs slowly. When the coating layer possesses a strongly polar character, more rapid release occurs.

The way of effecting the polymerization is known in the art. The acrylates or methacrylates used as coating materials are polymerized by a free radical mechanism. The polymerization may be a thermal polymerization using a peroxide as an initiator. Preferably, however, the polymerization is carried out under the influence of radiation, which initiates the formation of free radicals. The formation of radicals takes place, for example, directly through the use of electron beams (β -radiation) or of γ -radiation, but can also take place through the use of ultra-violet light. In the last-mentioned case preferably a photoinitiator is added to the coating material. The radiation techniques are known in the art. As photoinitiators to be used together with ultra-violet light, for example, known compounds, such as benzil ketals, benzoin ethers, acetophenone derivatives, ketoxime ethers,

benzophenone, benzil or thioxanthenes can be mentioned. These photoinitiators may be used, if necessary, together with co-initiators, such as aliphatic tertiary amines. In case of polymerization under the influence of radiation, the polymerization takes place rapidly at ambient temperature, so that heating is not necessary.

In the course of this process for coating substrates with polymers, which are formed in situ on the particles, a state also occurs where the coating is viscous and tacky. However, the period during which the critical viscosity range occurs is so small that the formation of agglomerates, and damage, hardly occurs. This period is in general less than 1 minute and amounts in many cases to 0.2 to 10 seconds, for example 0.5 to 1 second. Due to this extraordinarily rapid hardening of the coating layer, the coating process can be easily carried out continuously. If the coating layer is too thin or has inadequate mechanical strength, the coating process can be repeated once or several times, and in that case different coating materials can also be used for the different coating layers. In this way not only does the coating layer acquire the desired mechanical strength, but it is also possible to control the rate of release of the active substance from the substrate and to adjust it exactly for each separate active substance. By means of experiments, an expert can determine, with respect to each experiments, an expert can determine, with respect to each material to be coated and each coating material, the optimal control of the rate of release of the active substance from the substrate.

The coating of the substrate can be carried out continuously or discontinuously. For example, if a particulate material is to be coated, it can be mixed with the lacquer, while stirring cautiously, and subsequently the wet granules can be brought into a fluidized state above a glass filter through which nitrogen is passed. It is also possible to bring the particles to be coated into a fluidized state with the aid of a carrier gas and to introduce thereafter the lacquer used for the coating into the fluidized bed co-currently with the carrier gas, while the whole is subsequently exposed to radiation. The particles coated with the hardened lacquer are then removed from the fluidized bed. It may be noted in this context that the coating of fertiliser granules in a fluidized bed is known per se from German Patent Application 1,257,801 and German Patent Application 1,938,933.

In a number of cases it can be important that the release of the

active substance from the coated substrate should not take place immediately. It has been found that in a number of cases the coated substrate shows a certain induction period, that is to say a period in which it is already present in the particular environment in which
5 release of the active substance must occur, but during which no release as yet occurs. This can probably be ascribed to the fact that the coating layer must first be saturated with water from the environment in order that dissolution of the active substance from the substrate can begin. Induction periods of between 1 and 9 hours can readily be
10 achieved.

The following examples serve to illustrate the invention without limiting it to the embodiments shown.

Example I

A large number of tests was carried out with regard to the coating
15 of fertiliser granules with lacquers. The results of these tests are reported in Table A. The tests made use of the following starting materials:

Fertiliser

The fertiliser consisted of NPK 19-6-12.

20 Comparison materials

Osmocote, a product marketed by Sierra Chemical Europe B.V., fertiliser granules provided with a coating layer based on drying oils, dicyclopentadiene and maleic anhydride.

Ebecryl 170 PA, an acrylate derivative having a Höppler viscosity
25 of 5,200 mPa.s at 25°C.

Thinners

NVP, N-vinyl-2-pyrrolidone, a customary commercial product.

TPGDA, triisopropylene glycol diacrylate, a liquid having a hydroxyl number of less than 70, an acid number of less than 1 and a
30 Höppler viscosity of 10 - 20 mPa.s at 25°C.

HDDA, 1,6-n-hexanediol diacrylate, having a hydroxyl number of less than 25, an acid number of less than 1 and a Höppler viscosity of less than 10 mPa.s at 25°C.

Epoxy-acrylates

35 Ebecryl 605, a solution of 75% by weight of Ebecryl 600 in TPGDA. Ebecryl 600 is an oligomer of a straight-chain epoxy-acrylate, having a molecular weight of 500 and a Höppler viscosity of 4,000 mPa.s at 60°C.

Ebecryl 605 has a Höppler viscosity of 7,500 mPa.s at 25°C.

Ebecryl 1608, a solution of 80% by weight of Ebecryl 600 in OTA 480, having a Höppler viscosity of 1,000 mPa.s at 60°C.

VPS 1960, a prepolymer resin based on epoxidized soy bean oil, having an acid number of less than 20, a molecular weight of 1,200 and a
5 viscosity of 25,000 mPa.s at 25°C.

Photomer 3049, an aromatic epoxy-acrylic resin modified with fatty acid, having an acid number of 2 and a viscosity of 4,000 mPa.s at 60°C.

Urethane-acrylates

10 Ebecryl 204, a solution of 75% by weight of an aromatic urethane-acrylate in HDDA, having a Höppler viscosity of 17,000 mPa.s at 25°C and a molecular weight of 2,000.

Ebecryl 210, an aromatic straight-chain urethane-acrylate, having a Höppler viscosity of 3,500 mPa.s at 60°C and a molecular weight of
15 1,500.

Ebecryl 284, a solution of 88% by weight of an aliphatic urethane-acrylate in HDDA, having a Höppler viscosity of 7,500 mPa.s at 25°C and a molecular weight of 1,200.

Photomer 4094, an aliphatic trifunctional urethane-acrylate having
20 a viscosity of 100 mPa.s at 25°C and an acid value of 0.5.

Photomer 4127, an aliphatic difunctional urethane-acrylate, having a hydroxyl number of 40, an acid number of 0.5 and a viscosity of 14 - 20 mPa.s at 25°C.

Photomer 4149, an aliphatic trifunctional urethane-acrylate having
25 an acid number of 0.5 and a viscosity of 70 - 85 mPa.s at 25°C.

Polyester-acrylate

Laromer PE 55 F, a polyester-acrylate having a viscosity of 30,000 - 50,000 mPa.s and an acid number of less than 5.

Polyether-acrylate

30 A polyether-acrylate having two terminal acrylate groups, as a result of which it is crosslinkable via radical polymerization, was prepared by acrylating a polyether-diol, which contained one polypropylene oxide block, with a polyethylene oxide block on either side. The molecular weight of the polypropylene oxide block was 1,750
35 and the molecular weight of the polyethylene oxide blocks was 250 in total, so that the total molecular weight was 2,000. The polyether-diol described is commercially available under the trademark Pluriol PE 6100 (BASF, Ludwigshafen, Federal Republic of Germany).

Flow-out agent

Ebecryl 350, a polysiloxane diacrylate having a Höppler viscosity of about 250 mPa.s at 25°C. and an acid number of less than 1.

Ebecryl is a registered trademark of UCB, Drogenbos, Belgium.

5 VPS is a registered trademark of Degussa, Frankfurt, Federal Republic of Germany.

Photomer is a registered trademark of Diamond Shamrock Corporation.

10 Laromer is a registered trademark of BASF, Ludwigshafen, Federal Republic of Germany.

All the lacquer compositions used for the tests contained 4% by weight of the photoinitiator Irgacure 651 (a registered trademark of Ciba-Geigy, Basle), benzil-dimethylketal.

15 In all tests, the fertiliser granules were coated as follows with the lacquer. The lacquer was added to the granules, with cautious stirring. Thereafter, the wet granules were brought into a fluidized state on a glass filter through which nitrogen was passed. In this fluidized state, they were irradiated for 3 minutes by means of six
20 tubular low pressure mercury lamps emitting UV radiation between 300 and 460 nm. The fluidized state only occurs after the lacquer has partially hardened. In a number of cases, the coating with the lacquer, in the manner described, is repeated once or several times in order to restrict the effect of damage of the lacquer coating to a minimum. The thickness of the lacquer layer is shown in Table A.

25 After the fertiliser granules have been coated with the lacquer, the rate of release of the fertiliser from the granules to demineralised water is measured via the conductivity at 20°C. To that end, 150 ml of water are pumped continuously, by means of a peristaltic pump, at a speed of 35 ml per minute, through a bed of 30 g of granules
30 and through the measuring cell of a conductivity meter, by which the conductivity is continuously recorded. The rate of release is the mean rate of dissolution, measured in the period after the induction period, until 50% of the fertiliser originally present in the granules has dissolved. The rate of release is given as the weight of the fertiliser
35 dissolved per minute, expressed as a percentage of the weight of the fertiliser originally present in the granules.

Table A shows that the rate of release of the uncoated fertiliser is high, as was naturally to be expected. The Osmocote granules

provided or not provided with an additional lacquer coat, exhibit a very low rate of release.

The epoxy-acrylate lacquers used are themselves so viscous that they can only be employed when using a reactive thinner which is completely immobilized during hardening. Tests E1, E2, E3 and E4 show the influence of the viscosity of the lacquer on the quality of the hardened single lacquer coat. When using a lacquer which is too thin (test E1) or which is too thick (test E4), the rate of release was too high, due to lacquer damage. Using a more suitable viscosity (tests E2 and E3), the lacquer was less damaged, which manifests itself in a much lower rate of release.

Tests E5, E6, E7, E8 and E9 show that after the fertiliser granules have been coated with three layers of lacquer, these granules exhibit a fairly considerable release period, with the rate of release however being greater than that of the Osmocote granules, for which the induction period, on the other hand, is zero.

When using coatings based on urethane-acrylates it is found that the use thereof leads to greatly differing rates of release and induction periods. It appears that in tests U1 to U8 the rate of release is rather high, which is due to the low viscosity of the coating material used. In tests U9, U10, U11, U12, U13 and U14 low rates of release were obtained, which is due to the considerable higher viscosity of the coating material compared with tests U1 to U8. The acrylate content in these cases was however higher than the acrylate content in the epoxy-acrylate lacquers used. In these cases, however, an induction period does not always occur.

Tests U12 and U13 furthermore show that it is also possible to apply lacquer coats of different types in order to control the induction time and the rate of release. Test U14 gives an example of rate of release which is almost the same as that of the comparison material V2.

Test U13 shows that when using a flow-out agent (Ebecryl 350), a top coat having a very long induction period was formed, but on the other hand the rate of release was again somewhat higher.

When using the polyester-acrylate PE 55 F it is found that after 350 minutes the rate of release increases rapidly, namely from about 0.02 to about 0.07.

Table A shows clearly that it is possible for an expert to find the optimal coating for each particular case by performing simple tests.

Table A Influence of the lacquer coating composition on fertilizer granules on the induction period and release rate of these granules.
 - All lacquer coats contain 4% by weight of photoinitiator.

I Comparison materials

Test	Coat thickness, μm	Induction period, minutes	Release rate
V1 Uncoated fertilizer	0	0	20
V2 Osmocote	50	0	0.005
V3 Osmocote + Ebecryl 170 PA (0.033 g of lacquer/g of fertilizer)	60	0	0.00314

II Epoxy-acrylates

Test Type	Content, % by weight	Thinner	Content, % by weight	Number of coating steps	Loading, g of lacquer/g of fertilizer
E1 Ebecryl 605	25	NVP	71	1	10
E2 Ebecryl 605	61	NVP	35	1	10
E3 Ebecryl 605	79	NVP	17	1	10
E4 Ebecryl 605	87	NVP	9	1	10
E5 VPS 1960	24	TPGDA	72	3	50
E6 VPS 1960	48	TPGDA	48	3	50
E7 Ebecryl 1608	24	TPGDA	72	3	50
E8 Ebecryl 1608	48	TPGDA	48	3	50
E9 Photomer 3049	48	TPGDA	48	3	50
					75
					220
					150
					200
					160

Table A (continued)

III Urethane acrylates									
U1	Photomer 4127	78.5	NVP	17.5	2		0.033	10	2
U2	Photomer 4127	78.5	NVP	17.5	1		0.033	10	2
U3	Photomer 4127	96			1		0.033	10	2
U4	Photomer 4127	96			2		0.050	15	20
U5	Photomer 4127	96			3		0.033	10	20
U6	Photomer 4094	96			3		0.033	10	12
U7	Photomer 4149	96			3		0.033	10	5
U8	Photomer 4149	96			3		0.050	15	6
U9	Ehecryl 210	64	TPGDA	32	3		0.10	50	0
U10	Ehecryl 204	64	TPGDA	32	3		0.10	50	0
U11	Ehecryl 284	64	TPGDA	32	3		0.10	50	0
U12	Ehecryl 284	78	TPGDA	18	1		0.033	50	0.0086
	VPS	1960	78	18	2		0.066	50	0.014
U13	Ehecryl 284	78	TPGDA	18	1		0.033	50	0.020
	VPS	1960	78	16	2		0.066		
U14	Ehecryl 284	78	Ehecryl 350	2					
			HNDA	18	3		0.10	50	0.006
IV Others									
P1	PE 55 F	72	TPGDA	24	3		0.10	50	0.052
P2	Polyether-acrylate	78	HNDA	18	4		0.10	50	0.028

Example II

With the use of the coating method of Example I, but with a HPA 400 lamp (a medium-pressure metal halide lamp emitting UV radiation between 300 and 400 nm) as a radiation source granules of the commercial insecticidal and nematocidal composition Vydate 10 G[®] (E.I. du Pont de Nemours & Co.) were coated. This composition is a free-flowing granular product containing as the active compound 10% by weight of oxamyl, which has the chemical name methyl-N',N'-dimethyl-N- [(methylcarbamoyl)oxy]-1-thio- oxamimidate, which active compound is adsorbed on clay particles.

The test results are listed in Table B. The description of the coating materials can be found in Example I. Each of the coating compositions contained 4% by weight of the photoinitiator Irgacure 651. In each of the tests three coating steps have been used, in each of which the same quantity of lacquer was applied. In each test 15 g of Vydate 10 G particles have been coated and the coated particles have been examined. The release of the oxamyl was determined as follows: The coated particles were brought into demineralized water (10 parts by weight of water per part by weight of coated particles) and the release took place under static conditions. The content of oxamyl in the water phase was determined by high pressure liquid chromatography. The values of the release indicated in Table B are the amounts of oxamyl in the water phase as a weight percentage of the amount originally present in the composition.

From the results given in Table B it appears that already after 1 hour a considerable amount of oxamyl has been released so that by the use of the compositions coated according to the invention immediate protection against insects and nematodes is guaranteed. However, this protection is lasting much longer than the protection provided by the uncoated compositions from which the oxamyl has been released already completely after one hour. When comparing the results of tests 1-4 with the results of tests 5-8 it will appear that the release of oxamyl is retarded when the coat applied is thicker. However, finally all active substance is released in the course of time, which means that the lacquer does not prevent the active substance to leave the granule completely.

Table B

Test Type	Content % by weight	Thinner	Content % by weight	Number of coating steps	Loading g of lacquer/ g of Vydate 10 G	release (%) after			
						1 h	2 h	28 h	48 h
1	Ebecryl 605	NVP	79	3	0,3	52	62	80	95
2	Ebecryl 1608	TPGDA	48	3	0,3	53	53	57	85
3	Photomer 4127		96	3	0,3	50	54	55	87
4	Ebecryl 284	TPGDA	64	3	0,3	64	69	73	99
5	Ebecryl 605	NVP	79	3	0,25	59	76	85	100
6	Ebecryl 1608	TPGDA	48	3	0,25	50	65	65	95
7	Photomer 4127		96	3	0,25	76	75		98
8	Ebecryl 284	TPGDA	64	3	0,25	76	75	85	90
9	no coating (control)					100			

C L A I M S

1. A solid substrate, which consists at least partially of a biologically or chemically active substance and at least part of the surface of which is coated with a permeable network coating on the base of a water insoluble acrylic or methacrylic polymer.
- 5 2. A process for coating at least part of a solid substrate, which consists at least partially of a biologically or chemically active substance with a polymer, characterized by contacting the surface to be coated of the solid substrate with a coating material containing at least one polymerizable crosslinkable polyfunctional acrylic or
10 methacrylic compound and subjecting the coating material to polymerization substantially in the absence of non-polymerizable components.
3. Process according to claim 2, characterized in that in the coating material compounds having 2, 3 or 4 (meth)acrylate functions are
15 used.
4. Process according to claims 2 or 3, characterized in that one or more compounds of the group consisting of urethane-(meth)acrylates, epoxy-(meth)acrylates, polyester-(meth)acrylates, polyether-(meth)-acrylates and amine-(meth)acrylates are used in the coating material.
- 20 5. Process according to any one of the claims 2 to 4, characterized in that one or more monofunctional polymerizable monomers are incorporated in the coating material as modifier.
6. Process according to any one of the claims 2 to 5, characterized in that a coating material consisting of a liquid mixture of one or more
25 compounds of high viscosity and one or more compounds of low viscosity is used.
7. Process according to any one of the claims 2 to 6, characterized in that the coating material is polymerized under the influence of radiation, which initiates the formation of free radicals.
- 30 8. Process according to claim 7, characterized in that electron beams, gamma radiation or ultraviolet light are used.
9. Process according to claim 8, characterized in that ultraviolet light is used to effect the polymerization of the coating material and a photoinitiator is added to said coating material.

10. Process according to any one of the claims 2 to 9, characterized in that the substrate to be coated is a particulate solid material.

11. Process according to claim 10, characterized in that a polymer of the coating material is formed on the particles of the particulate material while said particles are in a fluidized state.

12. Process according to any one of the claims 2 to 11, characterized in that a material of the group consisting of drugs, flavouring substances, fragrances, agrochemicals, fertilisers, compositions containing a catalyst, compositions containing a microorganism and compositions containing an enzyme is coated.

13. Solid substrate coated according to anyone of the claims 2 to 12.



European Patent
Office

EUROPEAN SEARCH REPORT

0167184

Application number

EP 85 20 0620

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	US-A-3 857 932 (T.H. SHEPHER) * Column 2, line 42 - column 3, line 25; column 4, lines 14-16; column 5, lines 1-19 *	1-10, 12,13	C 05 G 3/00 A 61 K 9/32 B 01 J 2/30
X	GB-A-2 017 113 (JAPAN ATOMIC ENERGY RESEARCH INSTITUTE) * Page 2, lines 42-44, 59-64; page 3, lines 6-22; page 3, line 61 - page 4, line 2; page 4, line 65 - page 5, line 4; page 11, lines 5-17 *	1-10, 12,13	
A	CHEMICAL ABSTRACTS, vol. 96, no. 26, June 1982, page 369, no. 223179y, Columbus, Ohio, US; B. BOISRAMÉ et al.: "Use of acrylic film agents for coating in a fluidized bed of air", & BULL. SOC. PHARM. STRASBOURG 1980, 23(1), 97-106	11	
A	CHEMICAL ABSTRACTS, vol. 78, 1973, page 410, no. 28544q, Columbus, Ohio, US; & JP - A - 72 10 003 (MITSUI TOATSU CHEMICALS CO. LTD.) 25-03-1972		
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl. 4) C 05 G A 61 K B 01 J
Place of search THE HAGUE		Date of completion of the search 10-09-1985	Examiner VERHOEST J.P.M.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO Form 1500 (03/82)